Supplementary Materials: Electronic Communication between Dithiolato-Bridged Diiron Carbonyl and S-Bridged Redox-Active Centres

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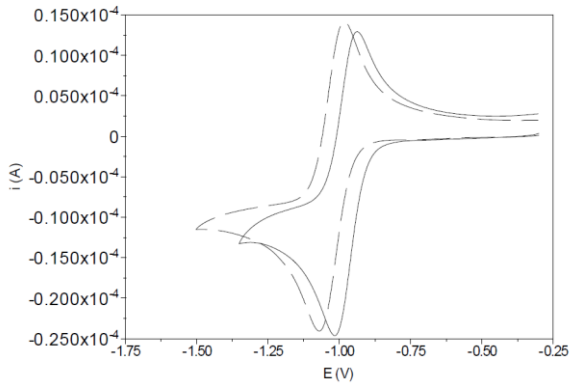

Figure S1 Cyclic voltammogram of (— —) nitrobenzene (2 mM) and (—) $CH_3C(CH_2S)_2CH_2S(C_6H_4$-p-$NO_2)$ (12) (2 mM) (0.2 M $[NBu_4][BF_4]$ in acetonitrile, 0.1 $V.s^{-1}$).

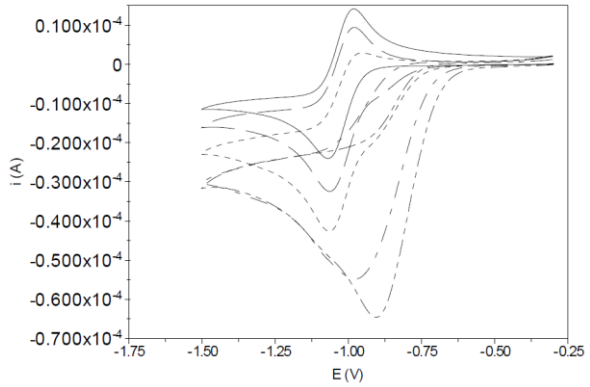

Figure S2. Cyclic voltammograms of the primary reduction processes of nitrobenzene (2 mM, 0.2 M $[NBu_4][BF_4]$ in acetonitrile, 0.1 $V.s^{-1}$) in the absence and in the presence of acetic acid: 0 (—), 1 (— —), 5 (---), 15 (– – – -) and 30 equivalents (— - - —).

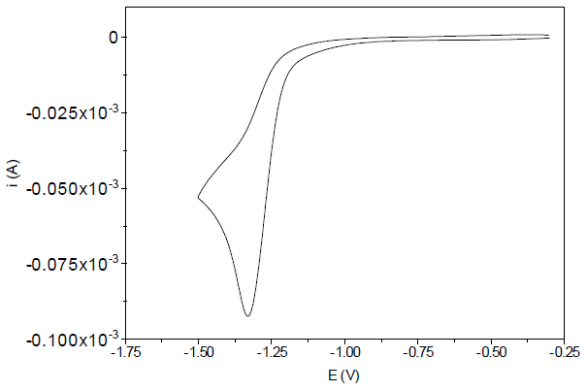

Figure S3. Cyclic voltammogram of 2,6-lutidinium tetrafluoroborate (0.4 M, 0.2 M $[NBu_4][BF_4]$ in acetonitrile, 0.1 $V.s^{-1}$).

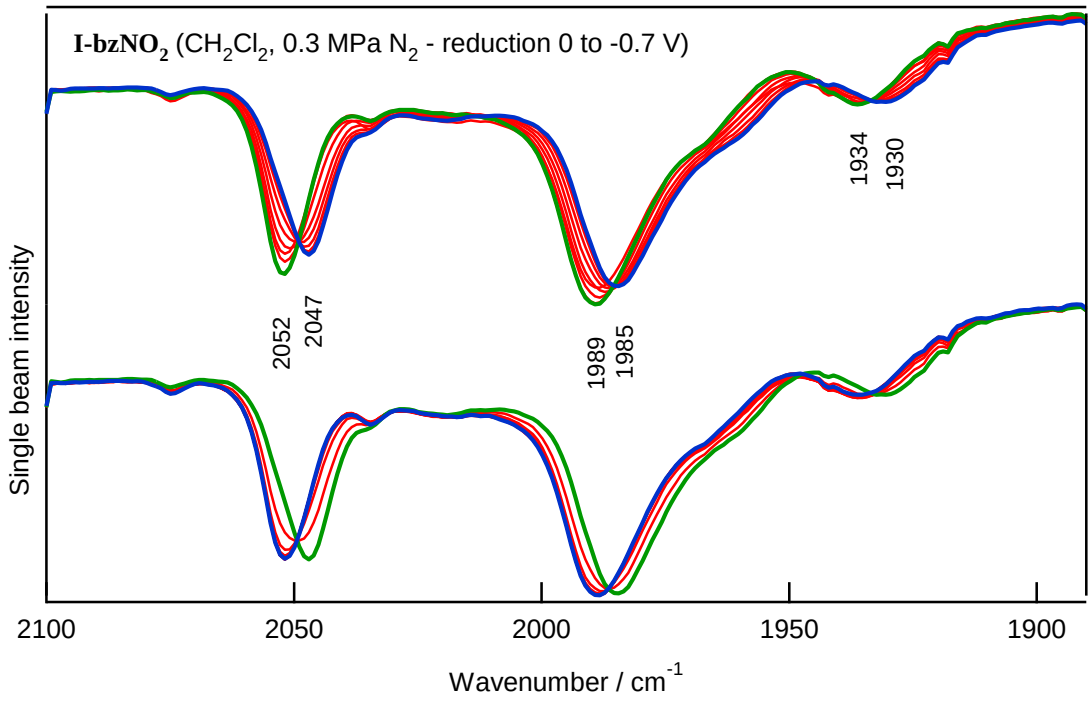

Figure S4. IR-SEC single beam spectra recorded during (top) reduction and (bottom) re-oxidation of **I-bzNO2** in CH_2Cl_2 (2 mM, 0.2 M $TBAPF_6$). For this, and subsequent, figures the initial spectrum of each block is shown in green and the final spectrum in blue.

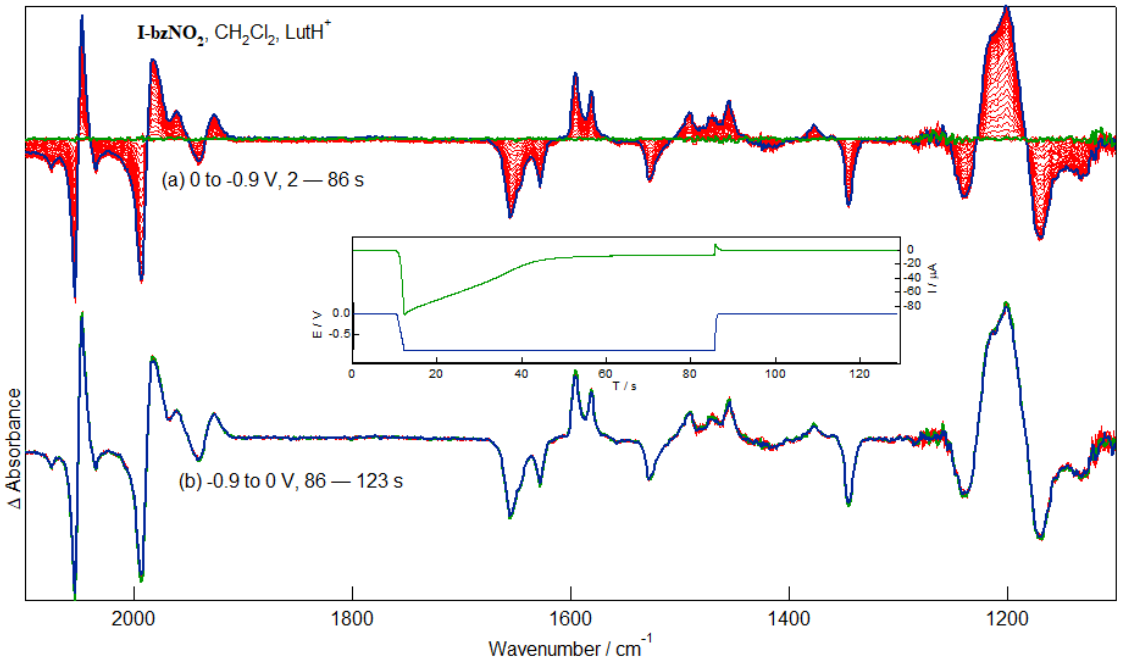

Figure S5. IR-SEC spectra recorded during (a) the reduction and (b) re-oxidation of **I-bzNO2** in the presence of $HLut^+$.

*Table S1. EasySpin EPR simulation parameters for [**I-bzNO$_2$**]$^-$.*

```
[Bexp,Espc,Params] = eprload('sb_fe2s3no2_hires_1');
Bexp = Bexp/10;
Be = Bexp .';
Bt = Be(3688:6145);
Esp = Espc .';
Espt = Esp(3688:6145);
g = (71.44775 * Params.MF) ./ Be;
Exp.mwFreq = Params.MF;
Exp.Range = [min(Bt) max(Bt)];
Exp.nPoints = size(Bt,1);
Sys.g = 2.00543;
Sys.Nucs = 'N, H, H, H, H, H';
Sys.n = [1 1 1 1 1 2];
Sys.lwpp = [0.08 0.036]*0.65;
An = 24.43;
Ah1 = 10.3;
Ah1p = 8.4;
Ah2 = 3.6;
Ah2p = 2.4;
Sys.A = [An, Ah1, Ah1p, Ah2, Ah2p, 1.4];
[Bsim,Sspc] = garlic(Sys,Exp);
Sspc = 1.5 * Sspc;
subplot(1,1,1), plot(Bt,Espt, Bsim,Sspc);
```

Table S2. Determination of the free energy activation ($\Delta G^{\ddagger}$) parameter in $CDCl_3$; T_c is the coalescence temperature; $\Delta\nu_{ab}$ is determined from the slow limit spectra.

Compound	$\Delta\nu_{ab}$ (Hz)	T_c (K)	$\Delta G^{\ddagger}$ (at T_c) (kJ.mol^{-1})	$\Delta G^{\ddagger}$ (at T_c) *simulated* (kJ.mol^{-1})	$\Delta H^{\ddagger}$ (kJ.mol^{-1})	E_a (kJ.mol^{-1})
I-bzNO$_2$	20-330*	200	/	38-42	/	/
I-bzNH$_2$	323	243	45.8 ± 0.5	45.80	51.7	55.4
I-bzNH$_3^+$	315	208	39.0 ± 0.5	38.98	14.2	16.2

* Due to the machine limitation it was not possible to record the slow limit spectra, however coalescence at approximately 200 K was observed and a range of value for $\Delta G^{\ddagger}$ was obtained by simulating the slow limit spectra using the programme *gNMR*.

NMR experiments were performed in *d*-chloroform and from the data activation energies $\Delta G^{\ddagger}$ for the AB↔A2 spin system of different {2Fe3S}-complexes were calculated at T_c and these are given in Table S1. Simulations of the NMR spectra were also performed and $\Delta G^{\ddagger}$ values (at T_c) are in very good agreement with the experimental data. Simulation of the spectra over a range of temperatures provides further data. $\Delta H^{\ddagger}$ are obtained from the Eyring plot (ln k/T vs. 1/T) and values of E_a are obtained from an Arrhenius plot (ln k vs. 1/T), noting that $\Delta H^{\ddagger} \approx E_a - RT$. In both cases, k values were estimated by simulation of the experimental spectra.